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(54) **NOX STORAGE CATALYST AND PROCESS FOR THE ABATEMENT OF NOX**

NOX-SPEICHERUNGSKATALYSATOR UND VERFAHREN ZUM REDUZIEREN VON NOX
CATALYSEUR DE STOCKAGE DE NOX ET PROCÉDÉ POUR LA RÉDUCTION DES NOX

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Description

TECHNICAL FIELD

5 **[0001]** The invention relates to a nitrogen oxide storage catalyst comprising a catalytic trap material and an NO_x storage material and a process for the abatement of NO_x in an exhaust gas stream generated by an internal combustion engine which periodically operates alternately between lean and stoichiometric or rich conditions.

BACKGROUND ART

10 **[0002]** Emission of nitrogen oxides ("NO_x") from lean-burn engines (described below) must be reduced in order to meet emission regulation standards. Conventional three-way conversion ("TWC") automotive catalysts are suitable for abating NO_x, carbon monoxide a ("CO") and hydrocarbon ("HC") pollutants in the exhaust of engines operated at or near stoichiometric air/fuel conditions. The precise proportion of air to fuel which results in stoichiometric conditions
15 varies with the relative proportions of carbon and hydrogen in the fuel. An air-to-fuel ("A/F") ratio of 14.65:1 (weight of air to weight of fuel) is the stoichiometric ratio corresponding to the combustion of a hydrocarbon fuel, such as gasoline, with an average formula CH_{1.88}. The symbol λ is thus used to represent the result of dividing a particular A/F ratio by the stoichiometric A/F ratio for a given fuel, so that; $\lambda = 1$ is a stoichiometric mixture, $\lambda > 1$ is a fuel-lean mixture and $\lambda < 1$ is a fuel-rich mixture.

20 **[0003]** Engines, especially gasoline-fueled engines to be used for passenger automobiles and the like, are being designed to operate under lean conditions as a fuel economy measure. Such future engines are referred to as "lean-burn engines". That is, the ratio of air to fuel in the combustion mixtures supplied to such engines is maintained considerably above the stoichiometric ratio (e.g., at an air-to-fuel weight ratio of 18:1) so that the resulting exhaust gases are "lean", i.e., the exhaust gases are relatively high in oxygen content. Although lean-burn engines provide enhanced fuel
25 economy, they have the disadvantage that conventional TWC catalysts are not effective for reducing NO_x emissions from such engines because of excessive oxygen in the exhaust. Attempts to overcome this problem have included operating lean-burn engines with brief periods of fuel-rich operation (engines which operate in this fashion are sometimes referred to as "partial lean-burn engines"). The exhaust of such engines is treated with a catalyst/NO_x sorbent which stores NO_x during periods of lean (oxygen-rich) operation, and releases the stored NO_x during the rich (fuel-rich) periods
30 of operation. During periods of rich (or stoichiometric) operation, the catalyst component of the catalyst/NO_x sorbent promotes the reduction of NO_x to nitrogen by reaction of NO_x (including NO_x released from the NO_x sorbent) with HC, CO and/or hydrogen present in the exhaust.

[0004] Diesel engines provide better fuel economy than gasoline engines and normally operate 100% of the time under lean conditions, where the reduction of NO_x is difficult due to the presence of excess oxygen. In this case, the catalyst/NO_x sorbent is effective for storing NO_x. As in the case of the gasoline partial lean burn application, after the NO_x storage mode, a transient rich condition must be utilized to release / reduce the stored NO_x to nitrogen. In the case
35 of the diesel engine, this transient reducing condition will require unique engine calibration or injection of a diesel fuel into the exhaust to create the next reducing environment.

[0005] NO_x storage (sorbent) components including alkaline earth metal oxides, such as oxides of Mg, Ca, Sr and Ba, alkali metal oxides such as oxides of Li, Na, K, Rb and Cs, and rare earth metal oxides such as oxides of Ce, La, Pr and Nd in combination with precious metal catalysts such as platinum dispersed on an alumina support have been used in the purification of exhaust gas from an internal combustion engine. For NO_x storage, baria is usually preferred because it forms nitrates at lean engine operation and releases the nitrates relatively easily under rich conditions. However, catalysts that use baria for NO_x storage exhibit a problem in practical application, particularly when the catalysts are
45 aged by exposure to high temperatures and lean operating conditions. After such exposure, such catalysts show a marked decrease in catalytic activity for NO_x reduction, particularly at low temperature (200 to 350°C) and high temperature (450°C to 600°C) operating conditions. In addition, NO_x absorbents that include baria suffer from the disadvantage that when exposed to temperatures above 450°C in the presence of CO₂, barium carbonate forms, which becomes more stable than barium nitrate. Furthermore, barium tends to sinter and to form composite compounds with support materials,
50 which leads to the loss of NO_x storage capacity.

[0006] NO_x storage materials comprising barium fixed to ceria particles have been reported, and these NO_x materials have exhibited improved thermal aging properties compared to the catalyst materials described above. EP 0 982 066 discloses the preparation of a catalyst comprising barium on ceria (powder) by impregnating. Said catalyst is used for the abatement of NO_x in an exhaust stream generated by an engine, which periodically operates alternately between
55 lean and rich conditions. Despite these improvements, there is an ongoing need to improve the performance of NO_x storage materials, particularly the ability of these materials to operate over a wide temperature range and to operate effectively after exposure to high temperature. It is also desirable to improve the kinetics of NO_x oxidation (required in advance of NO_x storage) and the kinetics of NO_x reduction (required following NO_x release). Thus, there is a need to

provide improved NO_x storage materials and methods for their manufacture.

SUMMARY

[0007] The present invention relates to a nitrogen oxide storage catalyst comprising a catalytic trap material comprising a catalytic component effective for promoting the reduction of NO_x under stoichiometric or rich conditions disposed on a refractory metal oxide support, and a nitrogen oxide storage material effective for absorbing the NO_x under lean conditions and desorbing and reducing the NO_x to nitrogen under stoichiometric or rich conditions, and a refractory carrier member, wherein the catalytic trap material is disposed on the refractory carrier member, and wherein the NO_x storage material is obtainable by mixing a solution of barium with the ceria particles, spray drying the particles, heating the spray-dried particles, and coating the particles on a substrate.

[0008] The nitrogen oxide storage material comprises ceria spray-dried particles having BaCO₃ or a mixture of BaCO₃ and MgCO₃ supported on the ceria particles wherein the NO_x storage material is obtainable by mixing a solution of barium with the ceria particles, spray drying the particles, heating the spray-dried particles and coating on a substrate.

[0009] Further, the present invention relates to methods of abating nitrogen oxide in an exhaust gas stream.

[0010] In certain embodiments, the coating of the nitrogen oxide storage catalyst further comprises at least one member of platinum group metals selected from the group consisting of platinum, palladium, rhodium, iridium and mixtures thereof supported on refractory oxide particles.

The refractory oxide particles may be selected from the group consisting of aluminum oxide, mixed aluminum oxide and zirconium oxide, mixed aluminum oxide and lanthanum oxide, mixed aluminum oxide and cerium oxide, mixed aluminum oxide and magnesium oxide, and alumina oxide mixed with one or more of zirconia and lanthana.

[0011] In a other embodiment the catalytic trap material includes a precious metal catalytic component effective for oxidizing NO to NO₂ under lean conditions and promoting the reduction of released NO_x to nitrogen under stoichiometric or rich conditions supported on a refractory metal oxide. Further described is a method of making a nitrogen oxide storage material comprising mixing a solution of barium with ceria particles, spray drying the particles, heating the spray-dried particles, mixing the composite particles with a precious metal supported catalyst and coating the slurry mixture of particles on a substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Fig. 1 is a graph showing the nitrogen oxide conversion efficiency of a catalyst in accordance with an embodiment of the invention and a comparative reference catalyst;

Fig. 2 is a graph comparing the nitrogen oxide storage capacity of various catalysts;

Fig. 3 is a graph comparing the nitrogen oxide storage capacity of catalysts;

Fig 4 is a graph comparing the nitrogen oxide storage capacity of two catalysts;

Fig 5 is a graph comparing the nitrogen oxide storage capacity of two catalysts; and

Fig 6 is a SEM image of the spray dried and calcined BaCO₃/CeO₂ composite material.

DETAILED DESCRIPTION

[0013] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0014] According to one or more embodiments of the invention, Ba sintering and Ba composite compound formation is reduced under the conditions of thermal stress in an exhaust gas of a lean burn engine. The NO_x storage material according to the present invention demonstrates improved NO_x storage capacity after thermal aging when used in a catalytic trap.

[0015] Described herewith are methods of manufacturing NO_x storage materials and catalytic traps including these storage materials

[0016] The present invention pertains to a process for abatement of NO_x in an exhaust gas stream generated by an internal combustion engine which periodically operates alternately between lean and stoichiometric or rich conditions, comprising locating the nitrogen oxide storage catalyst of the present invention in an exhaust passage of the engine and treating the exhaust gas stream with the catalyst whereby at least some of the NO_x in the exhaust gas stream is adsorbed by the nitrogen oxide storage catalyst during the periods of lean conditions and is desorbed from the catalytic trap and reduced to nitrogen during the periods of stoichiometric or rich conditions.

[0017] The refractory metal oxide support of the nitrogen oxide storage catalyst of the present invention may be porous

in nature and has a high surface area such as alumina, for example, gamma-alumina. Other suitable support materials include titania, titania-alumina, zirconia, zirconia-alumina, baria-alumina, lanthana-alumina, lanthana-zirconia-alumina, titania-zirconia, and mixtures thereof. Desirably, the refractory metal oxide support will have a surface area of between 5 and 350 m²/g, and more particularly between 100 and 200 m²/g. Typically, the support will be present on the coated substrate in the amount of 0.09 to 0.43 g/cm³ (1.5 to about 7.0 g/in³), for example between 0.18 and 0.37g/cm³ (3 and 6 g/in³). A suitable support material for the precious metal is alumina, which may be doped with one or more other materials. Alumina having a BET surface area of 200 m²/g and doped with 10%-30% ZrO₂ and 1%-4% LaO provided good results.

[0018] In one or more embodiments of the present invention the catalytic component preferably comprises a precious metal component, i.e., a platinum group metal component. Suitable precious metal components include platinum, palladium, rhodium and mixtures thereof. The catalytic component will typically be present in an amount of 0.71 to 7.06 g/l (20 to 200 g/ft³), more specifically, 2.11 to 4.23 g/l (60 to 120 g/ft³).

[0019] The NO_x storage material employed in the nitrogen oxide storage catalyst according to embodiments of the present invention comprises a spray-dried NO_x storage material comprising BaCO₃ supported on CeO₂ particles.

[0020] Examples of the refractory carrier member include, for example, stainless steel, titanium, aluminum zirconate, aluminum titanate, aluminum phosphate, cordierite, mullite and corundum. The carrier member may be employed as a monolithic honeycomb structure, spun fibers, corrugated foils, layered materials, etc.

[0021] In a gasoline vehicle application, a catalytic device employing a three-way conversion ("TWC") catalyst may be used in conjunction with the nitrogen oxide storage catalyst of the invention. Such a device will be located in an exhaust passage of the internal combustion engine and will be disposed upstream and/or downstream of the catalytic trap. The TWC catalyst would typically include platinum, palladium and rhodium catalytic components dispersed on a high surface area refractory support and may also contain one or more base metal oxide catalytic components such as oxides of iron, manganese or nickel. Such catalysts can be stabilized against thermal degradation by expedients such as impregnating an activated alumina support with one or more rare earth metal oxides, e.g., ceria. Such stabilized catalysts can sustain very high operating temperatures. For example, if a fuel cut technique is utilized, temperatures as high as 1050°C may be sustained in the catalytic device.

[0022] If the catalytic device is employed and is located upstream of the nitrogen oxide storage catalyst of the invention, the catalytic device would be mounted close to the exhaust manifold of the engine. In such an arrangement, the TWC catalyst would warm up quickly and provide for efficient cold start emission control. Once the engine is warmed up, the TWC catalyst will remove HC, CO and NO_x from the exhaust gas stream during stoichiometric or rich operation and HC and CO during lean operation. The nitrogen oxide storage catalyst of the invention would be positioned downstream of the catalytic device where the exhaust gas temperature enables maximum NO_x trap efficiency. During periods of lean engine operation, when NO_x passes through the TWC catalyst, NO_x is stored on the nitrogen oxide storage catalyst. The nitrogen oxide storage catalyst is periodically desorbed and the NO_x is reduced to nitrogen under periods of stoichiometric or rich engine operation. If desired, a catalytic device containing a TWC catalyst may be employed downstream of the nitrogen oxide storage catalyst of the invention. Such catalyst will serve to remove further amounts of HC and CO from the exhaust gas stream and, in particular, will provide for efficient reduction of the NO_x to nitrogen under periods of stoichiometric or rich engine operation.

[0023] In a diesel vehicle application, the catalytic NO_x-trap according to embodiments of the invention may be used in conjunction with a diesel oxidation catalyst (DOC), and a catalyzed soot filter (CSF); where the DOC and CSF are placed either before or after the catalyst of this invention. In another embodiment of the invention, it is possible to place the NO_x-trap catalyst directly onto the filter media.

[0024] The several components of the catalytic trap material may be applied to the refractory carrier member, i.e., the substrate, as a mixture of two or more components or as individual components in sequential steps in a manner which will be readily apparent to those skilled in the art of catalyst manufacture. A typical method of manufacturing the catalytic trap of the present invention is to provide the catalytic trap material as a coating or layer of washcoat on the walls of the gas-flow passages of a suitable carrier member. This may be accomplished, by impregnating a fine particulate refractory metal oxide support material, e.g., gamma alumina, with one or more catalytic metal components such as a precious metal, i.e., platinum group, compound or other noble metals or base metals, drying and calcining the impregnated support particles and forming an aqueous slurry of these particles. Spray-dried particles of the bulk NO_x sorbent may be included in the slurry. Alternatively, the NO_x storage material or sorbent may be dispersed into the support, preferably in an impregnation operation, as described below. Activated alumina may be thermally stabilized before the catalytic components are dispersed thereon, as is well known in the art, by impregnating it with, e.g., a solution of a soluble salt of barium, lanthanum, zirconium, rare earth metal or other suitable stabilizer precursor, and thereafter drying (e.g., at 110°C for one hour) and calcining (e.g., at 550°C for one hour) the impregnated activated alumina to form a stabilizing metal oxide dispersed onto the alumina. Base metal catalysts may optionally also have been impregnated into the activated alumina, for example, by impregnating a solution of a base metal nitrate into the alumina particles and calcining to provide a base metal oxide dispersed in the alumina particles.

[0025] The carrier may then be immersed into the slurry of impregnated activated alumina and excess slurry removed to provide a thin coating of the slurry on the walls of the gas-flow passages of the carrier. The coated carrier is then dried and calcined to provide an adherent coating of the catalytic component and, optionally, the catalytic trap material, to the walls of the passages thereof. The carrier may then be immersed into a slurry of fine particles of component of the NO_x storage material as a second or overlayer coating deposited over the layer of catalytic component. A magnesium component, e.g., a solution of a magnesium salt such as magnesium nitrate, acetate, sulfate, hydroxide, etc., may be combined with the slurry of component of the NO_x storage material or it may be applied as a third or overlayer coating deposited over the second layer of the NO_x storage material. The carrier is then dried and calcined to provide a finished catalyst trap member in accordance with one embodiment of the present invention.

[0026] Alternatively, the alumina or other support particles impregnated with the catalytic component may be mixed with bulk or supported particles of the NO_x storage material in an aqueous slurry, and this mixed slurry of catalytic component particles and NO_x storage material particles may be applied as a coating to the walls of the gas-flow passages of the carrier. Preferably, however, for improved dispersion of the NO_x storage material, the washcoat of catalytic component material, after being dried and calcined, is immersed (post-dipped) into a solution of a component (NO_x storage material precursor compound (or complex) and a magnesium precursor compound (or complex) to impregnate the washcoat with the NO_x storage material precursor. The impregnated washcoat is then dried and calcined to provide the NO_x storage material dispersed throughout the washcoat.

[0027] Separate discrete layers of washcoat may be applied in successive impregnating/drying/calcining operations, e.g., to provide a bottom washcoat layer containing a platinum catalytic component in a bottom washcoat layer and a palladium and/or rhodium catalytic component in a top washcoat layer. The NO_x storage material may be dispersed by impregnation into both the top and bottom layers.

[0028] In use, the exhaust gas stream which is contacted with the nitrogen oxide storage catalyst of the present invention is alternately adjusted between lean and stoichiometric/rich operating conditions so as to provide alternating lean operating periods and stoichiometric/rich operating periods. It will be understood that the exhaust gas stream being treated may be selectively rendered lean or stoichiometric/rich either by adjusting the air-to-fuel ratio fed to the engine generating the exhaust or by periodically injecting a reductant into the gas stream upstream of the catalytic trap. For example, the composition of the present invention is well suited to treat the exhaust of engines, including diesel engines, which continuously run lean. In such case, in order to establish a stoichiometric/rich operating period, a suitable reductant, such as fuel, may be periodically sprayed into the exhaust immediately upstream of the catalytic trap of the present invention to provide at least local (at the catalytic trap) stoichiometric/rich conditions at selected intervals. Partial lean-burn engines, such as partial lean-burn gasoline engines, are designed with controls which cause them to operate lean with brief, intermittent rich or stoichiometric conditions.

[0029] Described herewith is a nitrogen oxide storage catalyst comprising:

a coating on a substrate, the coating comprising a nitrogen oxide storage material comprising ceria particles having an alkaline earth oxide supported on the particles, the ceria having a crystallite size of between about 10 and 20 nm and the alkaline earth oxide having a crystallite size of between about 20-40 nm.

[0030] Preferably, according to the nitrogen oxide storage catalyst described, the coating further comprises at least one member of platinum group metals selected from the group consisting of platinum, palladium, rhodium, iridium and mixtures thereof supported on refractory oxide particles, wherein the refractory oxide particles are preferably selected from the group consisting of aluminum oxide, mixed aluminum oxide and zirconium oxide, mixed aluminum oxide and lanthanum oxide, mixed aluminum oxide and cerium oxide, mixed aluminum oxide and magnesium oxide, and alumina oxide mixed with one or more of zirconia and lanthana, wherein alternatively, it is preferred that the ceria particles have a particle size of between about 5 microns and about 50 microns and a BET surface area of between about 30 and 80 m²/g, and wherein preferably the ceria particles have an average pore volume of about 0.3 to about 0.5 ml/g, wherein more preferably the pores in the ceria particles have an average pore diameter of between about 3 nm and about 30 nm, and wherein it is further alternatively preferred that the catalyst exhibits improved nitrogen oxide storage capacity after aging at 850 °C for 50 hours at a stoichiometric air fuel ratio compared with a catalyst having non-spray-dried ceria particles with baria supported on the ceria particles.

[0031] Further described herewith is a method of making a nitrogen oxide storage material comprising mixing a solution of barium with ceria particles, spray drying the particles, heating the spray-dried particles, and coating the particles on a substrate.

[0032] Preferably, according to the method described the ceria particles have a surface area of between about 50 and about 150 m²/g prior to spray drying, more preferably the ceria particles has a particle size of between about 5 microns and about 20 microns and even more preferably the ceria particles have an average pore volume of about 0.3 to about 0.5 ml/g.

[0033] It is further preferred according to the method described that the pores in the ceria particles have an average

pore diameter of between about 3 nm and about 30 nm.

[0034] It is yet further preferred according to the method described that the nitrogen storage material exhibits an improved nitrogen oxide storage capacity after aging at 850° C for 50 hours at a stoichiometric air fuel ratio compared with a catalyst having non-spray-dried ceria particles with baria supported on the ceria particles.

[0035] Without intending to limit the invention in any manner, embodiments of the present invention will be more fully described by the following examples.

Example 1

Preparation of NO_x storage material

[0036] BaCO₃ and CeO₂ were intimately mixed and finely dispersed in a weight ratio of between about 1:3 and about 1:5. Cerium oxide having a BET surface area of between about 50-150 m²/g was mixed with a solution of barium acetate such that the BaCO₃/CeO₂ composite had a BaCO₃ content of about 10-30 wt%. After mixing, the suspension of soluble barium acetate and CeO₂ was then spray-dried at a temperature of between about 90°C and 120°C to obtain a solid mixture of barium acetate and ceria.

[0037] After spray-drying, the mixture was then heated at about 550°C to 800°C for about 2 hours to form particles of ceria having barium carbonate supported on the ceria particles. The resulting BaCO₃ had a crystallite size of between about 20 and 40 nm. The BaCO₃ and CeO₂ crystallites formed particles with a size of between about 5 and 50 microns. The BET surface area of the particulate mixture is between about 30 and 80 m²/g.

Preparation of Catalytic Component

[0038] To provide a fully formulated NO_x storage catalyst or catalytic trap as described above, in addition to the manufacture of barium carbonate supported on ceria, a precious metal can be supported on a refractory oxide according to the following description. Pt and Rh are impregnated onto Al₂O₃ by an incipient wetness procedure to yield 1.8 weight percent Pt and 0.1 weight percent Rh. Pd is impregnated separately onto alumina to a Pd loading of 1.4 weight percent.

[0039] A slurry mixture containing about 34 wt% of alumina previously mixed with Pt/Rh, about 9 wt% Pd on alumina, a solution of zirconium acetate with a content of about 3 wt% ZrO₂, magnesium acetate to yield 9 wt% MgO, and 45 wt% BaCO₃/CeO₂ spray-dried powder is milled at pH 6-8 until a particle size of 11 micron (d₉₀) is obtained.

Coating of a Substrate

[0040] Ceramic or metallic honeycomb substrates are coated with the slurry in a dip coating manner and then dried in a dryer and subsequently calcined in a furnace under air at about 450°C - 550°C. The coating procedure is then repeated until a loading of about 0.2-0.4 g/cm³ (4 - 6.5 g/in³) is achieved. The coating on the honeycomb catalyst comprises about 3 - 30 micron BaCO₃/CeO₂ particles and about 1 -20 micron alumina particles. BaCO₃ is fixed within the pores of the ceria particles in such a way that it does not migrate to the alumina particles. It is believed that the contact of BaCO₃ and alumina would lead to the formation of inactive Ba/Al₂O₃ composite compound formation upon aging, which has a reduced NO_x storage capacity compared to BaCO₃.

COMPARATIVE EXAMPLE 2

[0041] Samples were prepared in accordance with Example 1 above, except that the barium acetate/ceria solution was not spray dried.

EXAMPLE 3

NO_x Storage Capacity Testing

[0042] Two catalytic traps were prepared, a first catalytic trap was prepared in accordance with Example 1 and a comparative catalytic trap was prepared in accordance with Comparative Example 2. Both catalytic traps A were evaluated after aging for 8 hours at 850°C.

[0043] Both catalytic traps were evaluated as follows. An engine was set to an air/fuel ratio of 11.6 for 2 minutes at the desired temperature to remove all stored NO_x and oxygen from the catalyst. This mode represents rich engine operation. Subsequently, the engine was adjusted to an air/fuel ratio of 29.6 under constant NO_x mass flow. This mode represents lean engine operation. During the whole test, the NO_x concentration was measured before and after the NO_x trap using a NO_x analyzer.

$$U = \frac{NO_x^{massoutlet}}{NO_x^{massinlet}} \cdot 100 \quad (1)$$

[0044] After the 2 minute rich operation followed by a 60 second lean operation, the engine was set to a 3 second rich operation to remove stored NOx without having hydrocarbon and carbon monoxide tailpipe emissions. This 60 sec lean / 3 sec rich cycle is repeated 10 times to establish constant catalyst conditions. For the time period of the 10 lean/rich cycles the NOx efficiency (U) is calculated from the NOx inlet and NOx outlet concentrations via equation (1): NOx storage mass in g is calculated via equation (2):

$$NO_x^{mass}(g) = \int NO_x \cdot \dot{V} / V_{ideal} \cdot M_s \cdot 1 / (3.6 \cdot 10^6) dt \quad (2)$$

NOx = NOx concentration (ppm)

V = volume flow (m³/h)

V_{ideal} = ideal molar volume (l/mol) at STP

M_s = Molar weight of NO₂ (g/mol)

dt = time interval (s)

[0045] After the 10 lean/rich cycles, the engine is operated for 1 min rich to remove the stored NOx completely. Subsequently, the engine is operated under lean condition until no more NOx is stored in the trap. Under these conditions, the overall NOx storage capacity is evaluated. However, to achieve a NOx conversion of greater than 80%, the NOx storage capacity at high NOx efficiency is decisive. Figure 1 demonstrates that the NOx storage capacity of catalytic trap prepared in accordance with Example 1 utilizing a spray-drying process exhibited superior capacity compared to the Comparative reference Example.

EXAMPLE 4

Barium Concentration and Calcination Temperature

[0046] Different amounts of Ba were impregnated into ceria of different surface area, using the procedures described in Example 1. Ceria powders with different BET surface areas were used to determine the effect of the resulting Ba/Ceria composite powder.

[0047] Characterization of the impregnated powder included BET surface area measurement. In addition fully formulated NOx trap catalysts were prepared using the procedures described in Example 1 that contain the particular Ba/Ceria composite material as NOx storage component. The NOx storage properties of the catalysts have been evaluated after aging for 8 hours at 850°C under air with 10% H₂O in a laboratory reactor. The results are shown in Table I and Table II below.

[0048] Table I shows the result of a variation of the BaCO₃ and CeO₂ concentration together with a variation of the ceria used. After impregnation, all samples were calcined at 550°C in air to decompose the impregnated Ba precursor into BaCO₃.

TABLE I

Sample	BaCO ₃ Wt %	CeO ₂ wt %	BET Surface area of Cerla (m ² /g)	CeO ₂ Crystallite (nm)	BET Ba/Ceria calcined 4h 800°C (m ² /g)	BaCO ₃ Crystallite size As prepared (nm)	BaCO ₃ Crystallite size Aged, 4h 800°C (nm)	CeO ₂ Crystallite size of Ceria in Ba/Ceria aged 4h 800°C (nm)	Nox Storage at 300°C (g/l)	Nox Storage at 400°C (g/l)
A	29	71	90	12	13	20	34	28	2.8	2.4
B	29	71	40	18	9	22	30	34	1.4	2.0
C	25	75	66	16	14	21	32	28	2.6	2.7
D	20	80	90	12	17	22	40	27	3.5	1.9
E	20	80	40	18	13	20	26	31	2.3	2.4

[0049] After 800°C aging, the highest NO_x storage activity at 400°C is obtained with sample C, having a medium Ba concentration and a CeO₂ material with a medium BET surface area and crystallinity. A high BET surface area and relative low Ba concentration is especially beneficial for NO_x storage at 300°C. It is particularly interesting that sample D having the largest BaCO₃ crystallite size after aging yields the best NO_x storage at low temperature. In addition, increased Ba concentration resulted in decreased BET surface area and increase in CeO₂ crystal size.

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TABLE II

Sample	BaCO ₃ Wt %	CeO ₂ wt %	BET surface area of Ceia (m ² /g)	BaCO ₃ /Ceia calcination Temp °C (2h after spray drying)	BET Ba/ Ceia after calcination (m ² /g)	CeO ₂ crystallite size of Ceia in Ba/ Ceia (nm)	BaCO ₃ crystallite size after calcination (nm)	BET Ba/Ceria aged 4h 800°C (m ² /g)	BaCO ₃ crystallite sizeAged, 4h 800°C (nm)	CeO ₂ crystallite size of Ceria in Ba/ Ceria aged 4h 800°C (nm)	NOx storage at 300°C (g/l)	NOx storage at 400°C (g/l)
F	29	71	200	550	66	9	18	17	37	29	2.0	1.7
G	29	71	200	650	54	10	28	16	40	26	3.5	1.8
H	29	71	200	750	21	24	40	16	45	28	2.5	2.7
I	29	71	200	850	14	33	37	12	40	32	1.1	1.3

[0050] In order to determine an optimum BaCO₃/CeO₂ composite, the Ba/CeO₂ is calcined after Ba impregnation at different temperatures. This is done to decompose the Ba precursor to the carbonate and to conditioning the composite for optimum NO_x adsorption capacity. The data in Table II demonstrates that a calcination temperature between 550 and 750 °C after impregnation of Ba onto CeO₂ provided the best results for NO_x storage. The samples calcined within this temperature range had higher surface area and exhibited higher NO_x storage after aging than a sample calcined at 850°C. Furthermore, a BaCO₃ crystallite size of between about 20-50 nm, for example, 45 nm, and a CeO₂ crystallite size of between about 25-30 nm in combination with a sufficient BET surface area after aging yielded the highest NO_x storage at 400°C. According to the data in Tables I and II, an as-prepared BET surface area between 40-60 m²/g and a ceria crystal size between about 10- and 20 nm and a BaCO₃ crystallite size of between about 20-and 40 nm yielded the best performance after aging.

[0051] An example of a desirable morphology of spray dried and calcined BaCO₃/CeO₂ mixture is shown in the SEM image of Figure 6. Fig. 6 shows about 10-20 nm size CeO₂ crystals agglomerated to particles of about 5-50 microns in size. Adhering to these about 5-50 micron size CeO₂ particles are BaCO₃ particles of about 20 -150 nm size. The BaCO₃ particles are likely agglomerates of smaller crystallites.

EXAMPLE 5

Ceria Type and Doping

[0052] Various types of ceria and doping with different materials were evaluated for effect on BET surface area and decomposition temperature of the barium carbonate. The decomposition temperature is the temperature at which Ba reacts with ceria to form BaCeO₃. The samples below were prepared by an incipient wetness preparation instead of spray-drying prior to calcination. The results are shown in Table III:

TABLE III

Material	Decomposition Temperature of BaCO ₃ (°C)	BET surface as prepared (m ² /g)	BET surface after aging at 950°C (m ² /g)	phases observed by XRD after thermal treatment (950°C)
A (90% CeO ₂ , 10% La) +15% Ba	914	13	1.8	BaCeO ₃ , CeO ₂ , BaCO ₃
C (57% CeO ₂ , 43% Pr) +15% Ba	950	44	6	BaCeO ₃ , CeO ₂
D (72% CeO ₂ , 28% La) +15% Ba	770	31	6	BaCeO ₃ , CeO ₂
B (90% CeO ₂ , 10% La) +15% Ba (Example 5B)	945	30	6.6	BaCeO ₃ , CeO ₂ , BaCO ₃
E (95% CeO ₂ , 5% La) +15% Ba	945	25	10	BaCeO ₃ , CeO ₂ , BaCO ₃
F (90% CeO ₂ , 10% La) +15% Ba (Example 5F)	945	30	10	BaCeO ₃ , CeO ₂ , BaCO ₃
G (100%CeO ₂) +15% Ba	942	41	13	BaCeO ₃ , CeO ₂ , BaCO ₃
H (91 % CeO ₂ , 9% Pr) +15% Ba	950	86	16	BaCeO ₃ , CeO ₂

[0053] According to the data in table III, doping Ceria with La or Pr to a level of 10% does not influence the decomposition temperature of BaCO₃. Only sample D with 28% La has a much lower temperature of BaCO₃ decomposition while sample C even with 43% of Pr has a high resistance towards reaction with BaCO₃.

[0054] The preferred BaCO₃/CeO₂/dopant material should have a BET surface area >10m²/g after aging and a high resistance towards reaction to BaCO₃ as shown in table III.

EXAMPLE 6

Precious Metal Support

[0055] Various alumina supports were evaluated for stability. It was found that the support material for the precious metal tends to react with BaCO₃ at a certain temperature. If this temperature for a specific material is reached most or

all of the BaCO₃ has formed a compound with the support material and this compound has much diminished tendency to adsorb NO_x compared to BaCO₃.

[0056] The table below shows a list of different support materials derived from ZrO₂ or Al₂O₃. Materials A and B show higher BaCO₃ decomposition temperature than pure or La, Ba or ZrO₂ doped aluminas. However the surface area of those materials is relatively small compared to other doped or undoped materials. Furthermore, it was found that the higher the surface area of a material in presence of Ba the higher is the NO_x storage capacity of an aged catalyst containing this material.

[0057] In particular, it was found that ZrO₂ doped aluminas and also La and ZrO₂ doped materials have very thermally stable surface areas in presence of Ba. The preferred alumina should have a BET surface area of 150-250 m²/g, a pore volume of 0.3-0.8 ml/g an average pore size of 3-20 nm.

TABLE IV

	A1203/ZrO ₂ derived support + 15% BaO	Decomposition temperature of BaCO ₃ (°C)	BET surface as prepared (m ² /g)	BET after 4h 900°C	phases observed by XRD after thermal treatment
15	A (92%ZrO ₂ , 8% La ₂ O ₃)	820	36		BaZrO ₃ , BaCO ₃ , ZrO ₂
	B (31% MgO, 69% Al ₂ O ₃)	830	64	39	MgAl ₂ O ₄ , BaAl ₂ O ₄
20	C (20%Ba, 80% Al ₂ O ₃)	740	101.3	61	BaCO ₃ , BaAl ₂ O ₄
	D (4% La, 20% ZrO ₂ , 76% Al ₂ O ₃)	736	96		CeO ₂ , Al ₂ O ₃
	E (100% Al ₂ O ₃)	765	73.6	67.9	BaAl ₂ O ₄ , A1203, ZrO ₂
25	F (90% Al ₂ O ₃ +10% CeO ₂)	730	81	73	CeO ₂ , BaAl ₂ O ₄
	G (30%ZrO ₂ , 70% Al ₂ O ₃)	740	88		BaAl ₂ O ₄ , ZrO ₂
	H (20%Ba, 80% Al ₂ O ₃)	695	156	83	BaAl ₂ O ₄
30	I (82% Al ₂ O ₃ , 11% CeO ₂ , 7% ZrO ₂)	720	118	80	A1203, BaCO ₃
	J (100% Al ₂ O ₃)	720	116	106	BaAl ₂ O ₄
	K (72% Al ₂ O ₃ , 28% Mg)	750	130	100	MgAl ₂ O ₄ , BaAl ₂ O ₄ , BaCO ₃
35	L (90% Al ₂ O ₃ , 10% ZrO ₂)	700	133.5		BaAl ₂ O ₄ , Al ₂ O ₃
	M (80% Al ₂ O ₃ , 20% CeO ₂)	720	133	100	CeO ₂ , Al ₂ O ₃
40	N (80% Al ₂ O ₃ , 20% ZrO ₂)	720	121.7	100.5	Al ₂ O ₃ , ZrO ₂
	O (4 % La/ 15% ZrO ₂)	700	126		BaAl ₂ O ₄ , ZrO ₂ , A1203
	P (21 %Mg, 10% Zr, 69% Al ₂ O ₃)	730	142		BaCO ₃ , MgAl ₂ O ₄ , ZrO ₂
45	Q (97% Al ₂ O ₃ , 3% La)	720	152	121	Al ₂ O ₃
	R (75% Al ₂ O ₃ 25% ZrO ₂)	700	135		ZrO ₂ , A1203, BaCO ₃
	S (90% Al ₂ O ₃ 10% ZrO ₂)	700	154	124.1	Al ₂ O ₃ , BaCO ₃ , BaAl ₂ O ₄
50	T (85% Al ₂ O ₃ 15% ZrO ₂)	700	142		ZrO ₂ , Al ₂ O ₃ , BaCO ₃
	U (74,6%Al ₂ O ₃ , 0,4 % La/ 15% ZrO ₂)	748	156	132	BaAl ₂ O ₄ , Al ₂ O ₃ , ZrO ₂ , BaCO ₃

EXAMPLE 7

Optimization of Aged NO_x Storage Capacity

[0058] Various samples were tested for aged NO_x storage capacity for samples aged at 850° C in an oven with 10% steam in air. A sample prepared in accordance with comparative Example 1 having the NO_x sorbent samples with BaCO₃/CeO₂ concentration of sample C in Table I but spray dried and calcined to different surface areas as indicated (Example 7A = 41 m²/g and Example 7B = 52 m²/g). In addition, samples and B and F from table III were tested after spray drying with barium, preparing in accordance with Example 1 and aging in a laboratory reactor. The results shown in Fig. 2 demonstrate the spray dried and calcined material 7B, with a BET surface area of 52 m²/g exhibited the highest NO_x storage capacity, while the other samples had similar performance. According to these tests, there is no benefit associated with doping ceria with 10% of La.

[0059] Various samples were tested for aged NO_x storage capacity for samples aged at 850° C for 50 hours in an engine at stoichiometric air fuel ratio. In this case, the evaluation has been done at an engine. Samples prepared in accordance with comparative Example 2 (NO_x sorbent prepared by impregnation), by spray drying and by spray drying with optimized BET surface area were prepared. The results shown in Fig. 3 demonstrate the spray-dried sample exhibited superior results, particularly the sample with optimized BET surface area.

EXAMPLE 8

[0060] The effect of the refractory oxide to support the precious metal component of the catalyst was also tested. Samples N (Example 8A) and O (Example 8B) from Table IV above were prepared into fully formulated catalysts and tested for NO_x storage capacity after aging for 50 hours at 850° C under stoichiometric conditions. Fig. 4 shows that the lanthana and zirconia doped sample (Example O) exhibited the best results between 250 and 400° C. Similar results were observed for sample N aged 50 hours at 750° C (Example 8C) and sample O aged 50 hours at 750° C (Example 8D) at a lean air fuel ratio, and these results are shown in Fig. 5.

Claims

1. A nitrogen oxide storage catalyst comprising:

a catalytic trap material comprising a catalytic component effective for promoting the reduction of NO_x under stoichiometric or rich conditions disposed on a refractory metal oxide support, and an NO_x storage material effective for adsorbing the NO_x under lean conditions and desorbing and reducing the NO_x to nitrogen under stoichiometric or rich conditions, the NO_x storage material comprising spray-dried particles of ceria having BaCO₃ or a mixture of BaCO₃ and MgCO₃ supported on the ceria particles, and a refractory carrier member,

wherein the catalytic trap material is disposed on the refractory carrier member, and wherein, the NO_x storage material is obtainable by mixing a solution of barium with the ceria particles, spray drying the particles, heating the spray-dried particles, and coating the particles on a substrate.

2. The nitrogen oxide catalyst of claim 1, wherein the catalytic component comprises a precious metal component selected from the group consisting of platinum, palladium, rhodium, and mixtures thereof.

3. The nitrogen oxide catalyst of claim 1 or 2, wherein the refractory metal oxide support is selected from the group consisting of alumina, titania, titania-alumina, zirconia, zirconia-alumina, baria-alumina, lanthana-alumina, lanthana-zirconia-alumina, titania-zirconia, and mixtures thereof.

4. The nitrogen oxide catalyst of claim 3, wherein the refractory metal oxide is gamma-alumina.

5. The nitrogen oxide catalyst according to any one of claims 1 to 4, wherein the refractory carrier member is selected from the group consisting of stainless steel, titanium, aluminum zirconate, aluminum titanate, aluminum phosphate, cordierite, mullite, and corundum.

6. The nitrogen oxide catalyst according to any one of claims 1 to 5, wherein the refractory carrier member is in the form of a monolithic honeycomb structure, spun fibers, corrugated foils, or layered materials.

7. A process for the abatement of NO_x in an exhaust gas stream generated by an internal combustion engine which periodically operates alternately between lean and stoichiometric or rich conditions, comprising locating the nitrogen oxide storage catalyst according to any one of claims 1 to 6 in an exhaust passage of the exhaust gas stream.

Patentansprüche

1. Stickstoffoxid-Speicherkatalysator, umfassend:

ein katalytisches Fängermaterial umfassend eine katalytisch wirksame Komponente zur Förderung der Reduktion von NO_x unter stöchiometrischen oder fetten Bedingungen, die auf einem Träger aus feuerfestem Metall-Oxid angeordnet ist, und ein NO_x -Speichermaterial, das unter mageren Bedingungen das NO_x adsorbiert und unter stöchiometrischen oder fetten Bedingungen das NO_x desorbiert und zu Stickstoff reduziert, wobei das NO_x -Speichermaterial sprühgetrocknete Teilchen von Ceroxid mit BaCO_3 oder einer Mischung von BaCO_3 und MgCO_3 , das bzw. die auf den Ceroxidteilchen geträgert ist, umfasst, und ein feuerfestes Trägerelement, wobei das katalytische Fängermaterial auf dem feuerfesten Trägerelement angeordnet ist und wobei das NO_x -Speichermaterial dadurch erhältlich ist, dass man eine Lösung von Barium mit den Ceroxidteilchen mischt, die Teilchen sprühtrocknet, die sprühgetrockneten Teilchen erhitzt und die Teilchen auf ein Substrat aufträgt.

2. Stickstoffoxid-Katalysator nach Anspruch 1, wobei die katalytische Komponente eine Edelmetallkomponente ausgewählt aus der Gruppe bestehend aus Platin, Palladium, Rhodium und Mischungen davon umfasst.
3. Stickstoffoxid-Katalysator nach Anspruch 1 oder 2, wobei der Träger aus feuerfestem Metall-Oxid aus der Gruppe bestehend aus Aluminiumoxid, Titanoxid, Titanoxid-Aluminiumoxid, Zirkoniumoxid, Zirkoniumoxid-Aluminiumoxid, Bariumoxid-Aluminiumoxid, Lanthanoxid-Aluminiumoxid, Lanthanoxid-Zirkoniumoxid-Aluminiumoxid, Titanoxid-Zirkoniumoxid und Mischungen davon ausgewählt ist.
4. Stickstoffoxid-Katalysator nach Anspruch 3, wobei es sich bei dem feuerfesten Metall-Oxid um Gamma-Aluminiumoxid handelt.
5. Stickstoffoxid-Katalysator nach einem der Ansprüche 1 bis 4, wobei das feuerfeste Trägerelement aus der Gruppe bestehend aus nichtrostendem Stahl, Titan, Aluminiumzirconat, Aluminiumtitanat, Aluminiumphosphat, Cordierit, Mullit und Korund ausgewählt ist.
6. Stickstoffoxid-Katalysator nach einem der Ansprüche 1 bis 5, wobei das feuerfeste Trägerelement in Form von einer monolithischen Wabenstruktur, Spinnfasern, gewellten Folien oder Schichtmaterialien vorliegt.
7. Verfahren zur Verringerung von NO_x in einem Abgasstrom, der von einem periodisch zwischen mageren und stöchiometrischen oder fetten Bedingungen alternierend arbeitenden Verbrennungsmotor erzeugt wird, bei dem man den Stickstoffoxid-Speicherkatalysator nach einem der Ansprüche 1 bis 6 in einem Auslasskanal des Abgasstroms anordnet.

Revendications

1. Catalyseur de stockage d'oxyde d'azote comprenant :

un matériau de piège catalytique comprenant un composant catalytique efficace pour favoriser la réduction de NO_x dans des conditions stoechiométriques ou riches disposé sur un support d'oxyde métallique réfractaire, et un matériau de stockage de NO_x efficace pour absorber NO_x dans des conditions pauvres et désorber et réduire NO_x en azote dans des conditions stoechiométriques ou riches, le matériau de stockage de NO_x comprenant des particules séchées par atomisation d'oxyde de cérium comportant BaCO_3 ou un mélange de BaCO_3 et MgCO_3 supporté sur les particules d'oxyde de cérium, et un élément de support réfractaire, dans lequel le matériau de piège catalytique est disposé sur l'élément de support réfractaire, et dans lequel, le matériau de stockage de NO_x peut être obtenu par mélange d'une solution de baryum avec les particules d'oxyde de cérium, séchage par atomisation des particules, chauffage des particules séchées par atomisation,

et revêtement des particules sur un substrat.

2. Catalyseur d'oxyde d'azote de la revendication 1, dans lequel le composant catalytique comprend un composant de métal précieux choisi dans le groupe constitué du platine, du palladium, du rhodium, et de mélanges de ceux-ci.
3. Catalyseur d'oxyde d'azote de la revendication 1 ou 2, dans lequel le support d'oxyde métallique réfractaire est choisi dans le groupe constitué de l'alumine, l'oxyde de titane, oxyde de titane-alumine, oxyde de zircone, oxyde de zircone-alumine, oxyde de baryum-alumine, oxyde de lanthane-alumine, oxyde de lanthane-zircone-alumine, oxyde de titane-zircone, et des mélanges de ceux-ci.
4. Catalyseur d'oxyde d'azote de la revendication 3, dans lequel l'oxyde métallique réfractaire est la gamma-alumine.
5. Catalyseur d'oxyde d'azote selon l'une quelconque des revendications 1 à 4, dans lequel l'élément de support réfractaire est choisi dans le groupe constitué de l'acier inoxydable, le titane, le zirconate d'aluminium, le titanate d'aluminium, le phosphate d'aluminium, la cordiérite, la mullite et le corindon.
6. Catalyseur d'oxyde d'azote selon l'une quelconque des revendications 1 à 5, dans lequel l'élément de support réfractaire est sous la forme d'une structure de nid d'abeilles monolithique, fibres filées, feuilles ondulées ou matériaux stratifiés.
7. Procédé de diminution de NO_x dans un flux de gaz d'échappement généré par un moteur à combustion interne qui fonctionne périodiquement de façon alternée entre des conditions pauvres et stoechiométriques ou riches, comprenant la localisation du catalyseur de stockage d'oxyde d'azote selon l'une quelconque des revendications 1 à 6 dans un passage d'échappement du flux de gaz d'échappement.

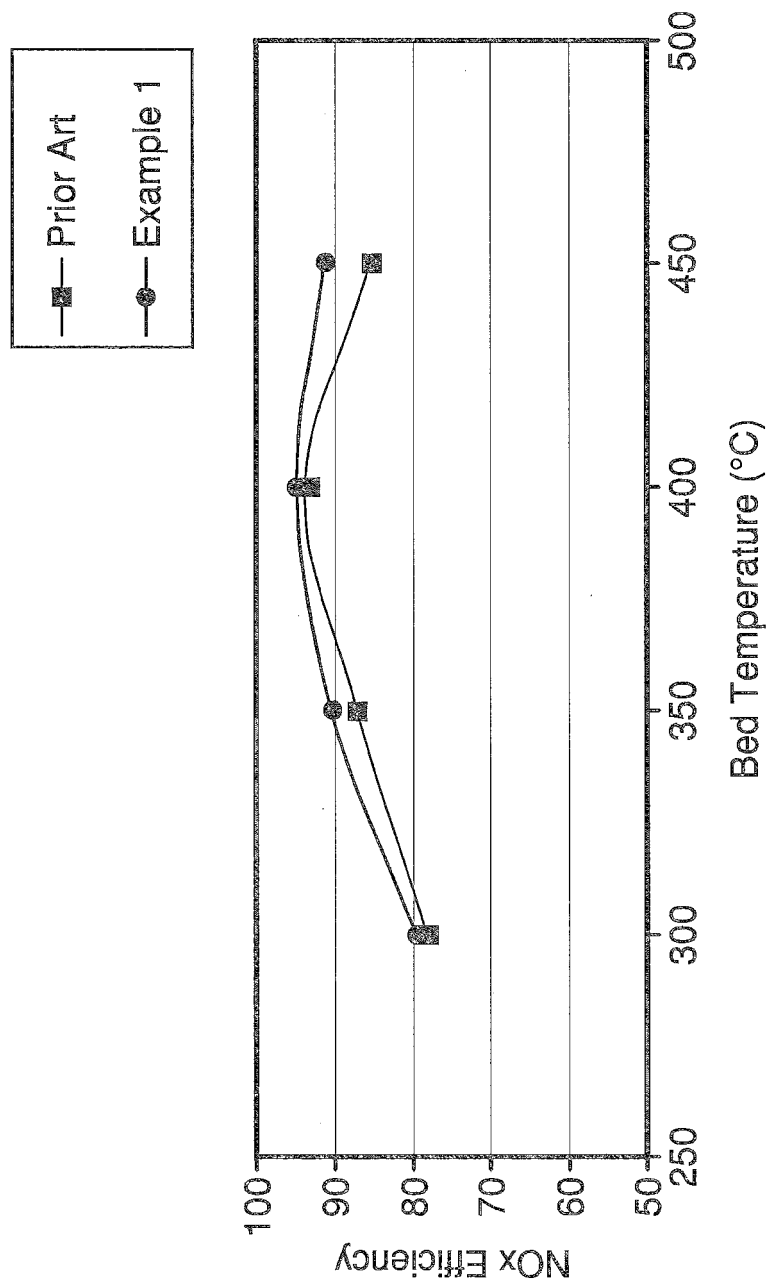


FIG. 1

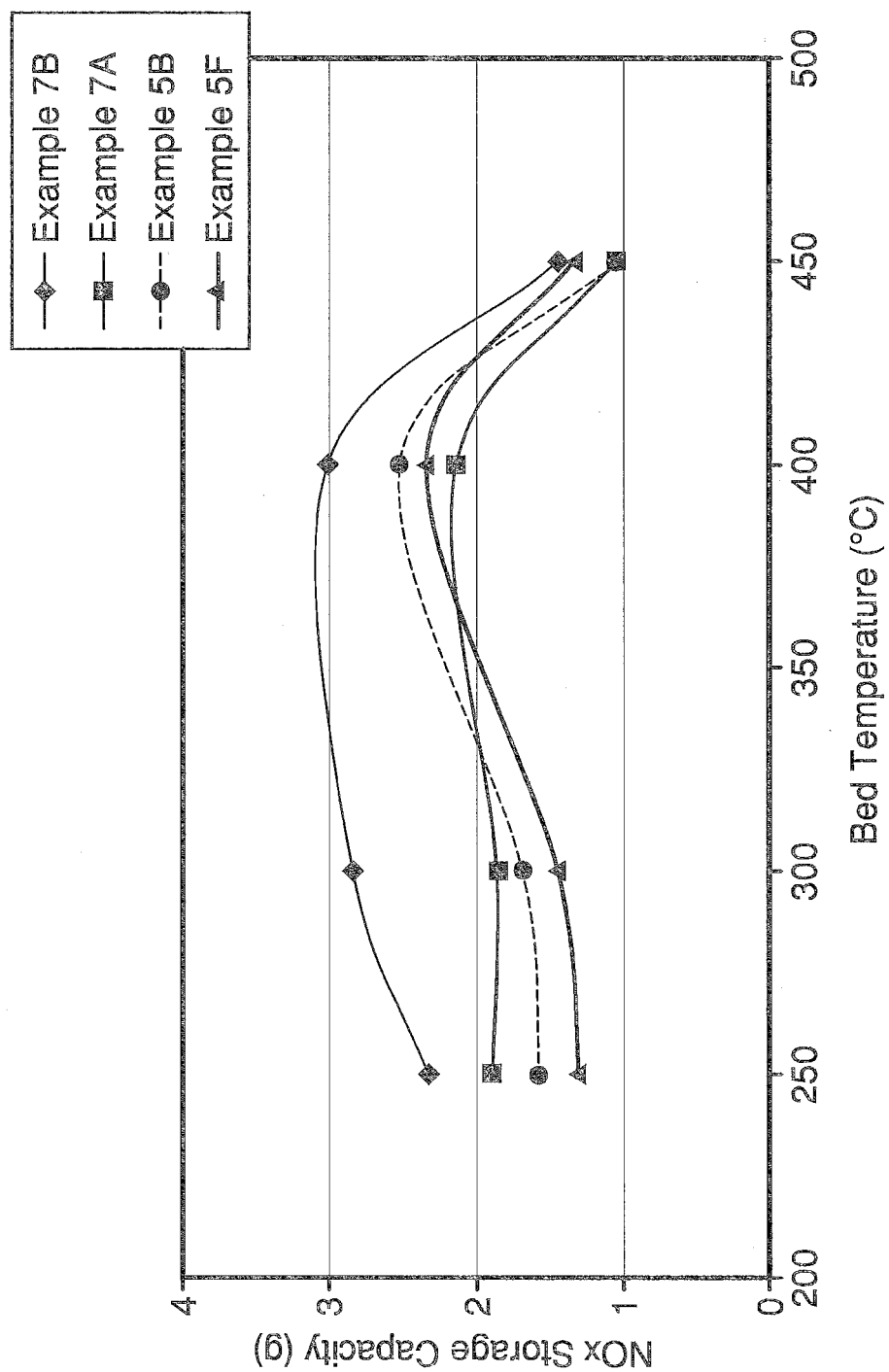


FIG. 2

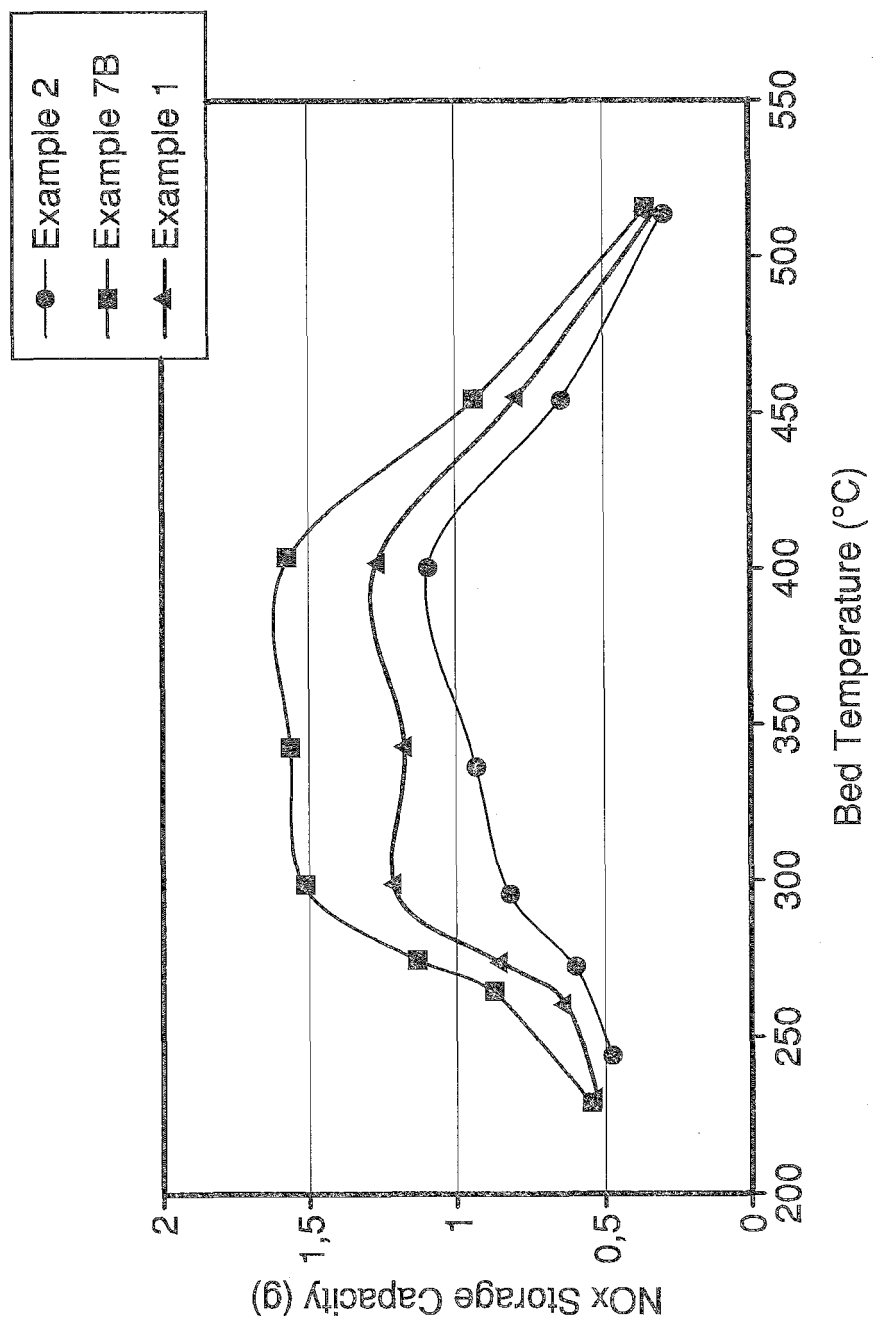


FIG. 3

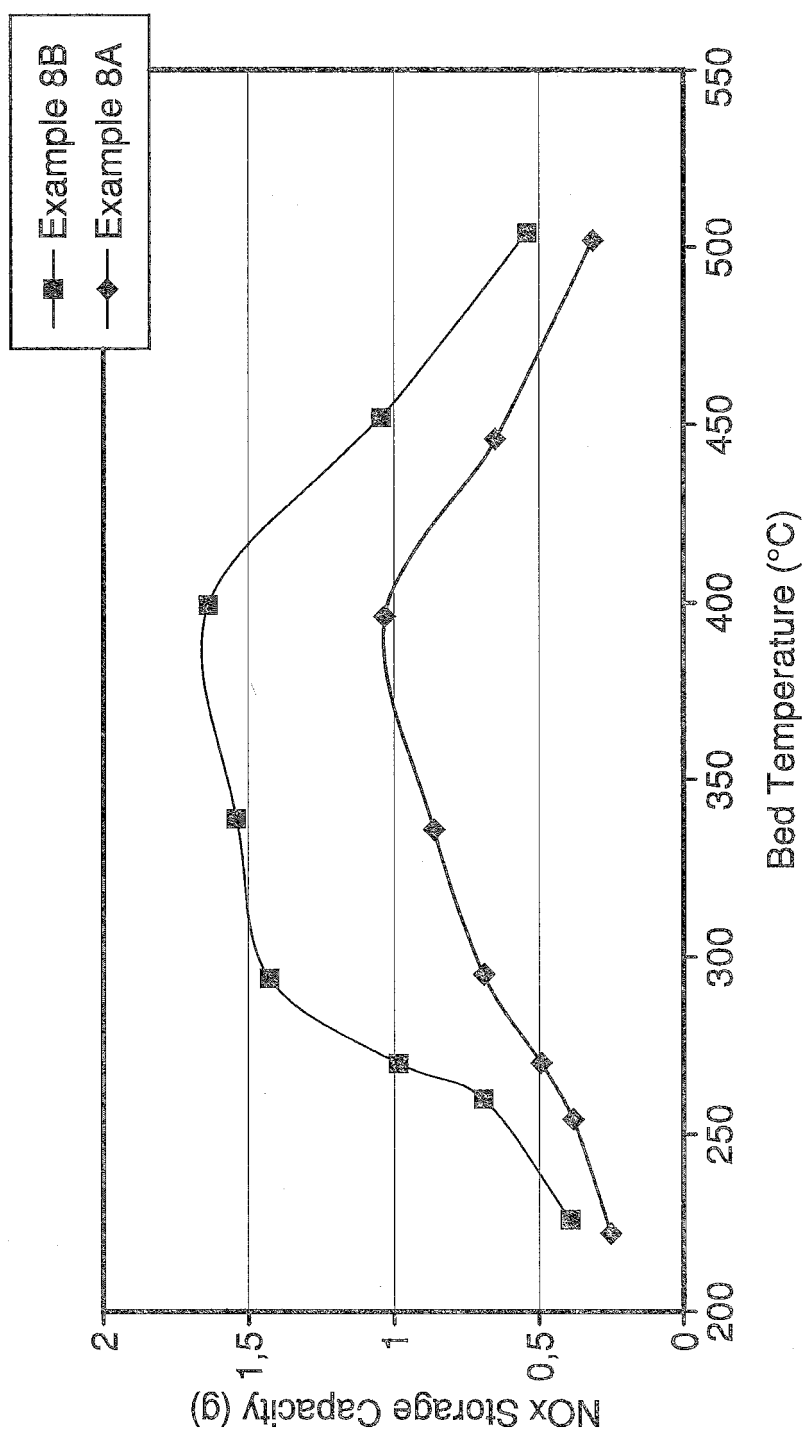


FIG. 4

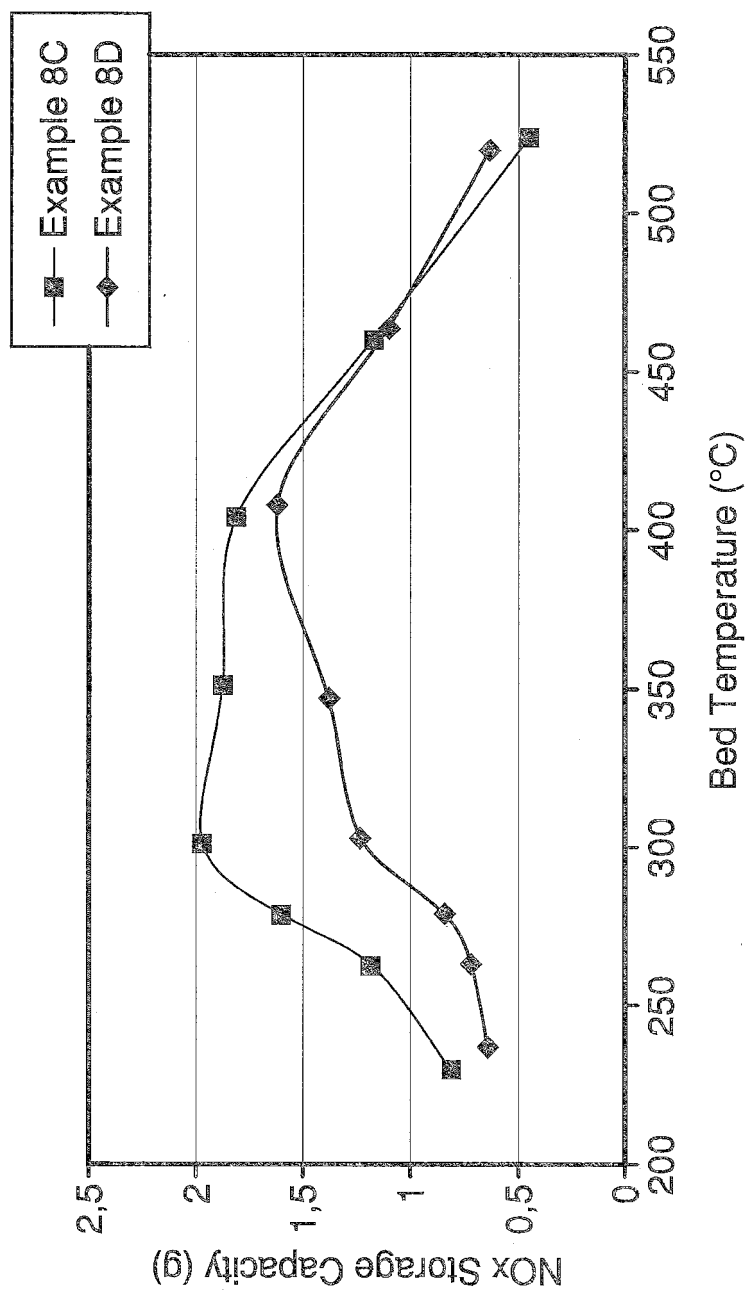


FIG. 5

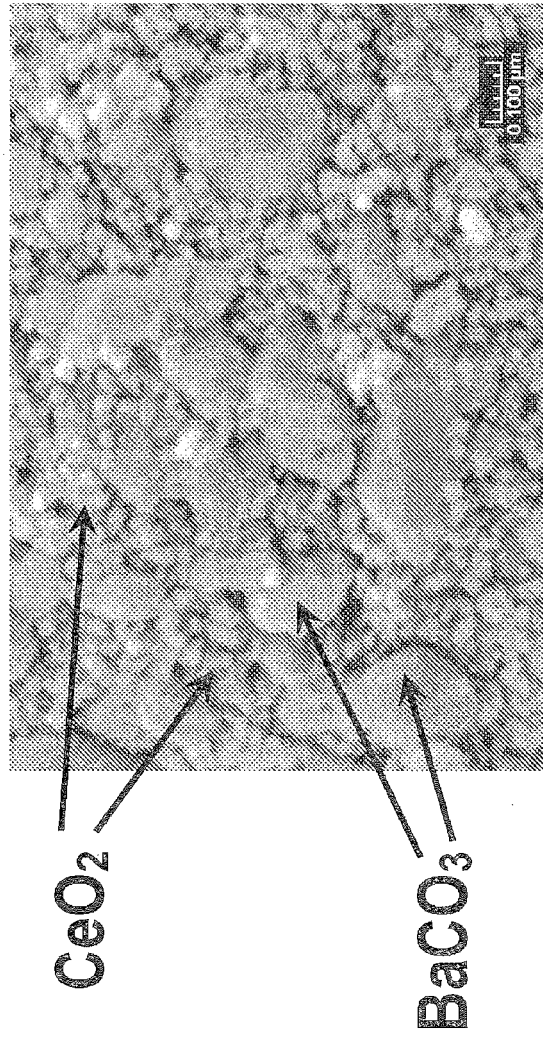


FIG. 6

REFERENCES CITED IN THE DESCRIPTION

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